

Note

Linearity of retention data plots for *n*-alkanes on porous silica in gas chromatography

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The method of Ševčík and Löwentap^{1,2} has been shown^{3,4} to provide a sensitive test of the linearity of plots of retention time *versus* carbon number for *n*-alkanes. For the accurate calculation of the adjusted retention time the ratio of the time differences for neighbouring *n*-alkanes in a homologous series was used. The ratio, *A*, of the antilogarithms of the slopes of the line between successive pairs of *n*-alkanes gives a measure of the constancy of the slope of the *n*-alkane line.

The linearity of the retention plots of *n*-alkanes has been studied using stationary phases of increasing polar character from SE-30 through OV-25 to Silar-7CP³. Values of calculated and experimentally determined retention times showed excellent agreement on all columns, indicating that the *n*-alkane lines are essentially linear. The values of *A* for all of the *n*-C₆–*n*-C₁₂ alkanes are indicative of complete linearity of the logarithmic plots. However, with the lower alkanes low *A* values are obtained for C₁–C₃ and high *A* values for the C₂–C₄ alkanes, indicating some curvature in the *n*-alkane plots for the gaseous species. The linearity has similarly been examined using the Porapak range of porous polymers⁴ and the same lack of linearity of the retention plots has been observed, particularly with the lower alkanes.

Porous silica beads of controlled texture provide an alternative material with applications in both gas–liquid and gas–solid chromatography. The materials reported by Guillemin and co-workers^{5–9} are produced by Pechiney-Saint-Gobain and marketed in Europe as Spherosil with representative grades being marketed by Waters Assoc. (Milford, MA, U.S.A.) as Porasils. Separations of permanent gases and of complex mixtures of various compounds have been described, together with studies in which coating with small amounts of stationary phases was used. Although the separation of various hydrocarbons has been demonstrated, retention measurements have not been reported.

In this work we examined the linearity of the graphs of retention time *versus* carbon number for a series of *n*-alkanes using a range of Porasil polymers.

EXPERIMENTAL

The equipment consisted of a Hewlett-Packard 5750 research chromatograph

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TABLE I
SURFACE AREAS AND POROSITIES OF PORASIL SAMPLES

Porasil grade	Surface area (m ² /g)	Pore diameter (Å)	Pore volume (cm ³ /g)	Spherosil designation
A	350-500	100	0.7-1.0	XOA 400
B	125-250	100-200	0.7-1.0	XOA 200
C	50-100	200-400	0.5-0.7	XOB 075
D	25-25	400-800	0.5-0.7	XOB 030

interfaced to a 16K PDP 11/40 computer. Interfacing was achieved by the use of an LPS 11 Laboratory Peripheral System consisting of a 12-bit analogue-to-digital converter, a programmable real-time clock with two Schmitt triggers and a display controller with two 12-bit digital-to-analogue converters. All on-line programming was written in CAPS II Basic with LPS options.

The retention times measured for the alkanes were used to calculate the dead times using the method of Grobler and Balizs¹⁰. This method has been demonstrated to be simple and accurate¹¹. The dead time, t_m , the slope, b , and intercept, C , were then used in eqn. 1 to estimate the uncorrected retention times, t_R , of the alkanes and methane:

$$\log(t_R - t_m) = bZ + C \quad (1)$$

where t_R is the uncorrected retention time of an n -alkane with carbon number Z .

The ratio, A , of the differences in retention times was calculated as an alternative method for assessing the linearity of the alkane line. The samples of Porasil (Waters Assoc.) had the characteristics shown in Table I^{8,12}. The beads were packed in PTFE columns (6 ft. × 1/8 in. O.D.) and operated as shown in Table II. A mixture of n -alkanes from methane to heptane in nitrogen was obtained from Commonwealth Industrial Gases (Alexandria, Australia).

RESULTS AND DISCUSSION

The results in Table II are for the injection of a mixture of C_1 - C_7 n -alkanes in nitrogen using a gas sampling valve, a technique previously shown^{3,4} to have a high precision for determining the retention times of the lower alkanes. The data in Table I indicate that the plot of retention time *versus* carbon number is non-linear for the lower alkanes, as shown by the A values calculated for the C_1 - C_3 and C_2 - C_4 n -alkanes. For the higher n -alkanes the A values assume greater constancy, although it is apparent that the values with Porasil A and B with the larger surface areas are most variable.

Table II also shows data for the alkanes using a column packed with Porasil C-10% squalane, and it is apparent that the performance of the compounds are hardly altered by use of a gas-liquid rather than gas-solid mode of separation.

In agreement with our earlier observations^{3,4} it is suggested that the use of methane retention for the determination of dead volume for columns packed with

TABLE II
RETENTION TIME DATA FOR C₁-C₇ *n*-ALKANES

Stationary phase	Conditions	<i>n</i> -Alkane	t_{exp}^* (sec)	t_{calc}^* (sec)	t'^* (sec)	<i>A</i>
Porasil A	Temperature, 100°C Helium, 50 ml/min; 5½ ft. × 1/8 in. PTFE; dead time = 42.3 sec	Methane	65.0	61.7	22.7	
		Ethane	85.0	81.1	42.7	1.70
		<i>n</i> -Propane	119.0	120.1	76.6	2.07
		<i>n</i> -Butane	189.5	198.2	147.2	2.04
		<i>n</i> -Pentane	333.0	354.7	290.7	2.05
		<i>n</i> -Hexane	627.0	668.3	584.7	2.10
		<i>n</i> -Heptane	1245.0	1297.1	1202.7	
Porasil B	Temperature, 80°C helium, 38 ml/min; 6 ft. × 1/8 in. PTFE; dead time = 52.4 sec	Methane	65.5	63.8	13.1	
		Ethane	77.5	75.4	25.1	1.75
		<i>n</i> -Propane	98.5	99.2	46.1	2.10
		<i>n</i> -Butane	142.5	147.5	90.1	2.07
		<i>n</i> -Pentane	233.8	245.8	181.3	2.08
		<i>n</i> -Hexane	424.0	445.7	371.6	1.99
		<i>n</i> -Heptane	821.5	852.1	769.1	
Porasil C	Temperature, 60°C helium, 50 ml/min; 6 ft. × 1/8 in. PTFE; dead time = 69.1 sec	Methane	80.5	79.8	11.5	
		Ethane	93.0	91.8	23.9	2.04
		<i>n</i> -Propane	118.5	119.3	49.4	2.25
		<i>n</i> -Butane	176.0	180.0	106.9	2.23
		<i>n</i> -Pentane	304.0	314.2	234.9	2.25
		<i>n</i> -Hexane	592.0	610.6	522.9	2.22
		<i>n</i> -Heptane	1231.0	1265.6	1161.9	
Porasil D	Temperature, 24°C; helium, 55 ml/min; 6 ft. × 1/8 in. PTFE dead time = 49.8 sec	Methane	53.3	53.6	3.5	
		Ethane	60.5	60.4	10.7	2.50
		<i>n</i> -Propane	78.5	79.1	28.7	2.96
		<i>n</i> -Butane	131.8	130.7	82.0	2.77
		<i>n</i> -Pentane	279.5	273.5	229.7	2.76
		<i>n</i> -Hexane	688.0	668.3	638.2	2.73
		<i>n</i> -Heptane	1802.0	1759.8	1752.2	
Porasil C-10% squalane	Temperature, 50°C; helium, 50 ml/min 6 ft. × 1/8 in. PTFE dead time = 109.7 sec	Methane	136.0	129.9	26.3	
		Ethane	164.5	157.2	54.8	2.04
		<i>n</i> -Propane	222.5	221.7	112.8	2.60
		<i>n</i> -Butane	373.0	373.4	263.3	2.37
		<i>n</i> -Pentane	730.0	730.9	620.3	2.37
		<i>n</i> -Hexane	1576.5	1572.6	1466.8	2.34
		<i>n</i> -Heptane	3556.5	3555.0	3446.8	

* t_{exp} , t_{calc} and t' are as defined previously³ and are respectively the experimentally uncorrected retention times, the calculated uncorrected retention times and the corrected retention times, calculated using the mathematical dead time, t_m .

both liquid and solid phases will lead to errors and the use of four *n*-alkanes of carbon C₄ and above is recommended. The behaviour of methane has recently been reported^{13,14} and effective carbon numbers less than unity have been suggested.

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REFERENCES

- 1 J. Ševčík, *J. Chromatogr.*, 135 (1977) 183.
- 2 J. Ševčík and M. S. H. Löwentap, *J. Chromatogr.*, 147 (1978) 75.
- 3 M. S. Wainwright, J. K. Haken and D. Srisukh, *J. Chromatogr.*, 188 (1980) 246.
- 4 M. S. Wainwright, J. K. Haken and D. Srisukh, *J. Chromatogr.*, 198 (1980) 156.
- 5 A. J. de Vries, M. Le Page and C. L. Guillemin, *Anal. Chem.*, 39 (1967) 935.
- 6 C. L. Guillemin, M. Le Page, R. Beau and A. J. de Vries, *Anal. Chem.*, 39 (1967) 940.
- 7 C. L. Guillemin, W. Deluil, S. Cirendini and J. Vermost, *Anal. Chem.*, 43 (1971) 2015.
- 8 C. L. Guillemin, M. Le Page and A. J. de Vries, *J. Chromatogr. Sci.*, 9 (1971) 470.
- 9 S. Cirendini, J. Vermont, J. C. Gressin and C. L. Guillemin, *J. Chromatogr.*, 84 (1973) 21.
- 10 A. Grobler and G. Balizs, *J. Chromatogr. Sci.*, 12 (1974) 57.
- 11 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 147 (1978) 65.
- 12 *Bull.*, No. 27258, Waters Assoc., Milford, MA, Nov. 1974.
- 13 J. F. Parcher and D. M. Johnson, *J. Chromatogr. Sci.*, 18 (1980) 267.
- 14 M. S. Wainwright and J. K. Haken, *J. Chromatogr.*, 256 (1983) 193.